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IMPROVEMENT OF THE PROCESS FOR ELECTROCHEMICAL  
IMPREGNATION OF NICKEL HYDROXIDE ELECTRODES

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16. Abstract Nickel hydroxide electrodes containing about $11\text{g/dm}^2$ of hydroxide, with capacities of 3.6 to 3.8 Ah/dm <sup>2</sup> may be prepared at 353°K by electrochemical impregnation. The reproducibility of the results are obtained by readjusting the pH before each preparation. The control of each electrode is done during two cycles of charge and discharge following the manufacture by means of a potential relaxation method.			
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## IMPROVEMENT OF THE PROCESS FOR ELECTROCHEMICAL IMPREGNATION OF NICKEL HYDROXIDE ELECTRODES

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### INTRODUCTION

Nickel-cadmium batteries are known for their great reliability. /129\* However when used for long periods of time under trying conditions such as those found in space applications, failures may occur. Their causes are very schematically associated with degradation of the solution in potash, with the appearance of a complex ion soluble in cadmium II and of variations in the size of the nickel hydroxide electrode. During cycling and especially if the discharge is deep, the structure of the nickel hydroxide prepared by chemical precipitation of the  $\beta$  crystallographic phase is converted. This causes the electrode to expand and may lead to hydroxide particles at the bottom of the battery and to a partial drying of the separator.

The electrochemical impregnation process (1-3) consists of promoting a local variation of the pH inside a porous nickel support, by electrochemical reduction of the  $\text{NO}_3$  ions, allowing the hydroxide to precipitate. This is an attractive process because it theoretically involves the preparation of the most voluminous  $\alpha$  phase. The plates obtained by electrochemical impregnation thus have a much greater dimensional stability than those obtained by chemical impregnation. Also, the electrochemical efficiency of such a hydroxide is about 30% greater than that of a chemically prepared hydroxide.

Yet, despite the technical and financial efforts offered by numerous companies, it was not possible to lead to an industrialization of the process. This is likely due to the abundance of parameters involved in the preparation and to the inadequate control

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\*Numbers in the margin indicate pagination in the original text.

of some of these which leads to major irreproducibilities in the quality of the electrodes prepared.

The work presented concerns the influence of a few of these factors on the laboratory preparation of electrochemically impregnated electrodes and on the adaptation of electromechanical methods for assuring their control.

## 1. Equipment and Methods

### a) Preparing the Plate

The electrolysis cell is thermoregulated, impervious and provided with a water circulation condenser. The electrodes prepared are 65x38mm, and predesigned on a nickel strip covered with sintered nickel by coating. The anodes are massive nickel electrodes deposited on either side of the cathode at a distance of about 10 mm. The electrical wiring is potentiostatic and the variation in the cathode potential is monitored in time with respect to a reference electrode made of saturated calomel (e.c.s.) connected to the cell by a LUGGIN capillary.

Impregnation occurs at 80°C with a current density of 7.5 A/dm<sup>2</sup> and an Ni(NO<sub>3</sub>)<sub>2</sub> 3M and Co (NO<sub>3</sub>)<sub>2</sub> electrolytic solution in various concentrations whose pH is adjusted to the required value by adding nitric acid or soda. Impregnation is done until a cathode potential of -0.8 volt (e.c.s.) is obtained and causing reduction in the solvent.

The electrode prepared is then profusely rinsed in distilled water, drained, immersed in a 7.2 M potash solution at ambient temperature, placed between two plates of massive nickel 8 mm apart. It is subjected to a charge with a current density of 6A/dm<sup>2</sup> for one hour, followed by a discharge at a current density of 1.5 A/dm<sup>2</sup> until a zero potential is obtained with respect to an electrode of the second type (Hg/HgO/OH<sup>-</sup>).

## b) Characterization of the Plate

The electrode is charged at a constant intensity at the rate of C/5 for 7 hours (40% overcharge) and the amount of energy re-stored during the discharge at constant intensity (C/5 or C) is measured until a zero potential is obtained with respect to the Hg/HgO/OH<sup>-</sup> electrode. At least two cycles of this type were made.

The impregnation rate is determined by weighing the electrode following the qualification cycles after abundant washing in distilled water and stove drying for one hour at 70°C. The mass variation  $\Delta P$  before and after impregnation gives the quantity deposited. The assumption made consists of omitting the metallic nickel loss due to corrosion and the results are presented by adopting the formula  $\text{Ni}(\text{OH})_2, 2/3 \text{H}_2$  for the deposited hydroxide.

## 2 RESULTS

A large number of tests were conducted to obtain a current density allowing electrodes to be prepared rapidly which contain at least 10 g/dm<sup>2</sup> hydroxide and exhibiting capacities of about 3.5 Ah/dm<sup>2</sup>. Moreover we aimed for a low enough operating temperature to allow the use of fairly volatile deposition additives. The most important parameter in this context for obtaining a good reciprocity of the results is the pH which should be readjusted to 2.5 after each impregnation.

Other general conclusions are that cobalt does not seem to have much influence on the performance of plates, at least during the initial cycles.

The presence of formic acid does not cause a modification of the characteristics of the plates prepared. However one sees a decline in the dissolution rate of the anodes. Hydrochloric acid makes it possible to avoid an easy passivation of these anodes and

a concentration of 0.1 M in  $\text{Cl}^-$  ions makes it possible to bring about a drop in the voltage at the terminals of the impregnation cell by more than one volt and to reduce the plate preparation time by a factor between 2 and 3. No deposit is seen on the anodes during their operation, but one does notice an acceleration in the dissolution of these electrodes.

During an impregnation the bath composition is monitored by spectrophotometric measurements which shows that for optimized tests the nickel nitrate concentration may be considered to be constant during impregnation and virtually no nitrite ions form which allows us to assume that the mechanism complies more with SEIGER's (4) or HAUSSLER's (5) proposals than with those of MAC ARTHUR (6).

### 3. USE OF A RELAXATION METHOD FOR CONTROLLING PREPARED PLATES

#### a) Description of the Method (7,8,9)

The method consists of collecting and analyzing variations in the potential of an electrode, identified in terms of a reference electrode as a function of the time of an intensity in the electrolysis circuit after interruption.

This method is semi-empirical, based on the observation that there is a linear relationship between the potential and logarithm of time and that all time potential curves obtained for a given system are superposed by a shift in the time scale.

Based on these two observations the law proposed is  $\frac{dE}{dt} = \frac{k}{t+\theta}$ .  $E$  is the theoretical time it would take for the potential to decrease from infinity to the value  $E_0$  just before interruption of the current density. By calling  $E^*$  the potential of the electrode at time zero we have:

$$E = E^* + k \ln \theta - k \ln (t + \theta)$$

Experimentally the value of  $k$  is the slope of TAFEL's straight line  $b$ . It is actually possible to find this empirical equation by representing the electrode by a capacitor with capacity  $C_d$  (double layer, adsorption capacity, etc.) in parallel with a charge transfer resistor  $R_T$ , by assuming that at the time of current interruption the electrode process continues in an open circuit by transferring through the capacity which is assumed to be constant according to a mechanism identical to that which existed when the current passed through. For example for an oxidation process and assuming there is a quick substance transfer at the interface, we have at the initial instant;

$$\left(\frac{dq}{dt}\right)^* = -C_d \left(\frac{d\eta}{dt}\right)^* = i^* + I_0 \exp\left(\frac{\eta}{b}\right)$$

equations in which  $q$  is the quantity of electricity which passes through the electrode,  $i_0$  the transfer current density,  $\eta$  the over-voltage and  $b$  the slope of TAFEL's straight line defined by  $\eta = a \pm b \ln i$ . At instant  $t$   $\frac{dq}{dt} = -C_d \frac{d\eta}{dt} = i_0 \exp\left(\frac{\eta}{b}\right)$  whose integration leads to  $\eta = \eta^* + b \ln \frac{bC_d}{i^*} - b \ln\left(t + \frac{bC_d}{i^*}\right) - b \ln\left(t + \frac{bC_d}{i^*}\right)$  with  $\eta \rightarrow \infty$  when  $t \rightarrow \left(-\frac{bC_d}{i^*}\right)$ .

In practice, this consists of recording in 20 to 30 seconds the variation of the potential as a function of time and by iterations to look for the value of  $\theta$  which leads to the linear relationship between  $E$  and  $\ln(t+\theta)$  with the best correlation coefficient. The measurements are performed with a plate which is electrochemically impregnated in the same cell as that used for capacity measurements with a potash solution of 7.3 M. They are performed during the charge and discharge cycles of the electrode.

## b. Results

They are shown in figures 1 to 3. Figure 1 shows an example of experimental results which make it possible to determine the



the equilibrium potential  $E_R$  which is not accessible by direct determination. If one avoids charges which are too rapid, overcharges and a prolonged contact with potash, this measurement is reproducible and is not influenced by the current density employed or the presence of dissolved oxygen in the solution.

The measurement of the equilibrium potential for the  $\alpha$  Ni(OH)<sub>2</sub>/ $\gamma$  NiOOH system is 0.411V (% Hg/HgO/OH<sup>-</sup>4M) and for the  $\beta$  Ni(OH)<sub>2</sub>/ $\beta$  NiOOH system is 0.429 V (% Hg/HgO/OH). These values are very close to those proposed in the reference [10]. Figure 2 shows the variation of the parameter b during the charge of the electrode, and figure 3 the influence of the impregnation rate on parameter b in the 40%, 80% charge range.

Although this semi-empirical method is not suitable for a detailed study of the mechanism for obtaining nickel hydroxide, it is still simple to use and full of information on the electrode prepared. It makes it possible to estimate the charge condition with good accuracy in the 30% - 80% charge range by first calibrating one of these. The measurement is more accurate when the set of electrodes is impregnated in similar operating conditions, although parameter b is not very sensitive to variations in the composition of active matter and of the impregnation rate (figure 3).

With the precision in determining the equilibrium potential, it is possible to know the crystallographic structure of the hydroxide deposited without extra handling. One simply needs to record and process a relaxation curve for the charge and one for the discharge during a conditioning cycle.

Calculation of the pseudo-capacity Cd makes it possible to estimate the impregnation rate  $\Delta P$ , but the accuracy is not as great as that obtained with b. It is therefore necessary to perform several relaxation measurements and take the mean value. In these conditions, one may hope to obtain  $\Delta P$  with an error of less than 2 g/dm<sup>2</sup>.

## CONCLUSION

The set of results presented show that it is possible to obtain reproducible results on battery plates measuring some 20 square centimeters of surface enclosing  $11\text{g/dm}^2$  of nickel hydroxide and having capacities of  $3.6\text{ Ah/dm}^2$ , which were measured during the first cycles. The potential relaxation method is proven to be effective for controlling the condition of the electrode charge and the type of hydroxide deposited. Perhaps the traditional procedure for preparation should be modified. According to this method one continuously prepares strips charged with nickel hydroxide in which one then cuts out the plates. One of the reasons for the irreproducibility of the materials prepared is perhaps because it is difficult to assure the homogeneity of the hydroxide over the entire length of the strip. Replacement of the traditional procedure by a procedure whereby one would prepare the electrode itself and whereby one would assure its quality is conceivable. /132

One method of preparing plates which are controlled at the end of the production line using a potential relaxation method should undoubtedly generate the best reproducibility in preparing nickel hydroxide electrodes.

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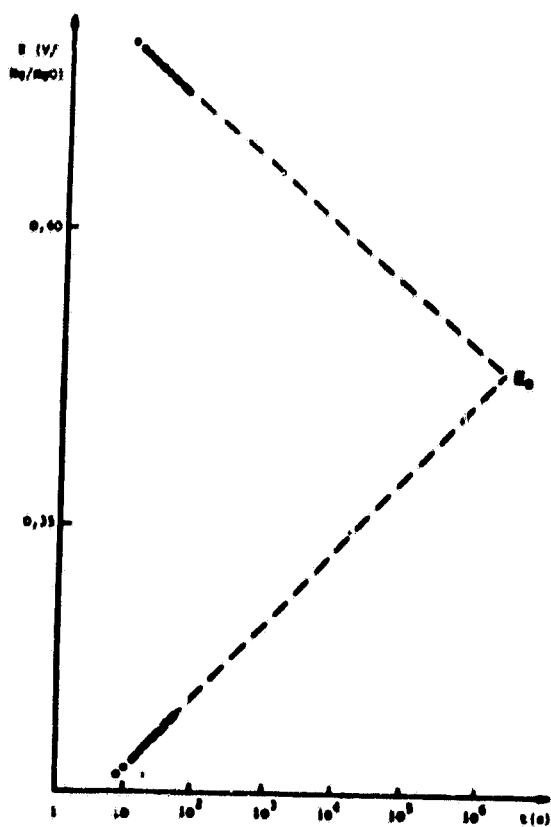


Figure 1 - Determination of the Equilibrium Potential of a Nickel Hydroxide Electrode. KOH 8M solution. Electrode in 40% charge range.

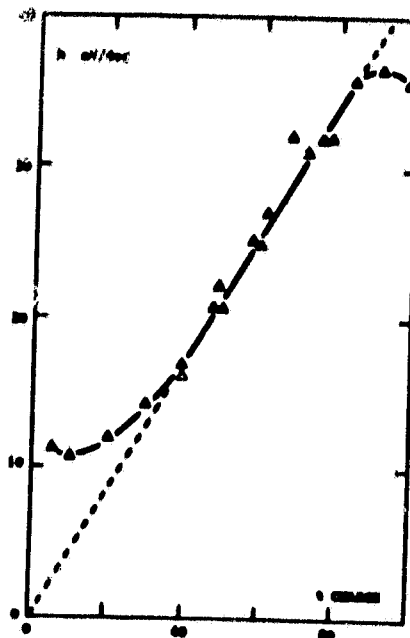
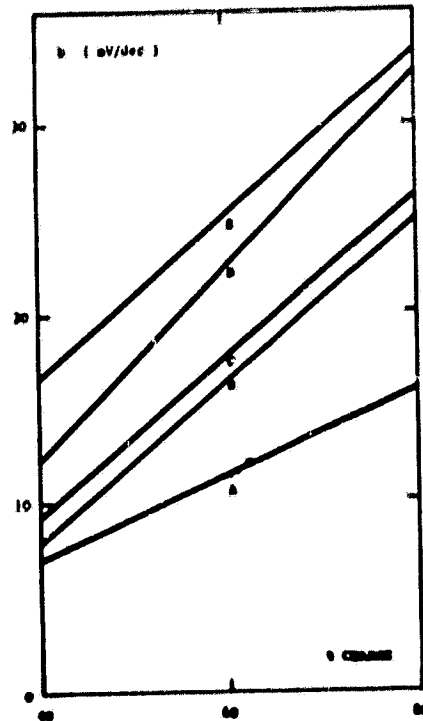


Figure 2 - Variation of b parameter (slope of TAFEL's straight line as a function of the electrode charge.



A :  $AP = 2,53 \text{ g/da}^2$   
 B :  $AP = 4,71 \text{ }^{\circ}$   
 C :  $AP = 6,13 \text{ }^{\circ}$   
 D :  $AP = 6,19 \text{ }^{\circ}$   
 E :  $AP = 11,63 \text{ }^{\circ}$

Figure 3 - Impact of the Impregnation rate on the parameter  $b$  (slope of TAFEL's straight line) in the 40% - 80% charge range.